Silicon Defect and Impurity Studies Using Controlled Samples

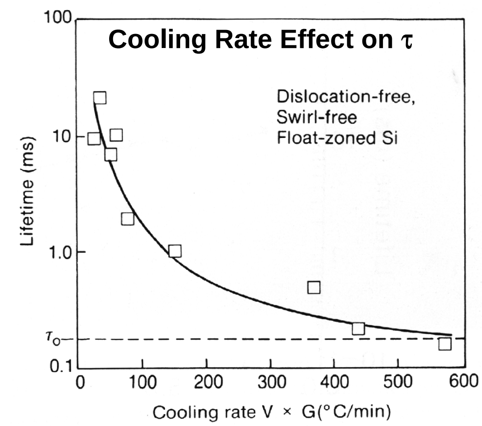
Ted F. Ciszek

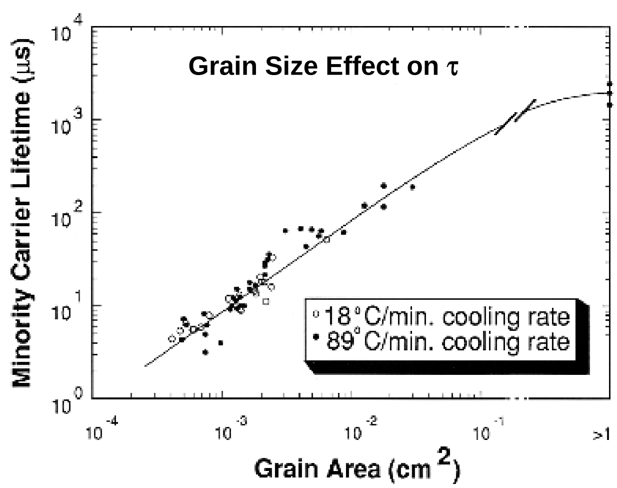
National Center for Photovoltaics
National Renewable Energy Laboratory, Golden, CO, 80401 USA
Phone (303) 384-6569/FAX (303) 384-6531/E-Mail ted_ciszek@nrel.gov

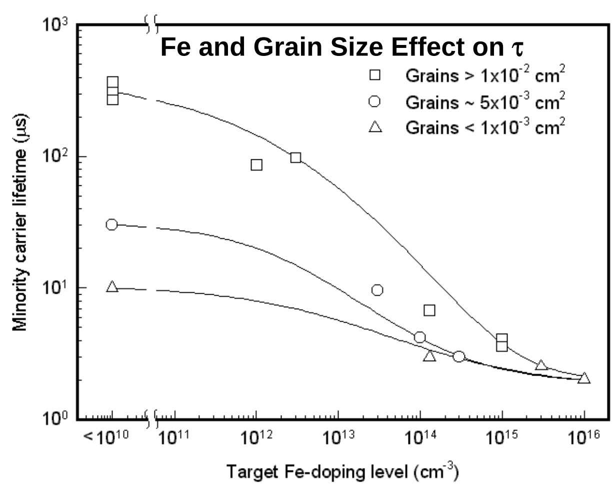
Because diverse defects and impurities are typically present in any given sample of silicon material, it can be extremely difficult to conduct a controlled study of the influence of any particular defect or impurity on photovoltaic properties such as minority charge carrier lifetime τ or solar cell efficiency η. For example, the influence of iron may be different if boron is present. Therefore it is important to conduct such studies on controlled samples where the influence of secondary effects is minimized.

The high-purity float-zone (FZ) growth method was used to obtain controlled samples. Because there is no crucible or other heated components, very high purities and low defect levels can be achieved in baseline material. The baseline can be controllably perturbed by introduction of specific defects or impurities. The chart shown below lists some of the types of defect and impurity combinations that can be studied in this way. The boxes marked with an “x” represent combinations we have examined over the past several years and will summarize in this presentation. The three figures convey some of our findings.

	IMPURITIES					
DEFECTS	---	O	C	N	H	Fe
Vacancy defects (D)	x			x	x	
Si self interstitials (I)	x			x	x	
Type B swirl defects	x			x	x	
Type A swirl defects	x			x	x	
Twins						
Dislocations	x					
Slip						
Lineage						
Grain Size	x			x		x

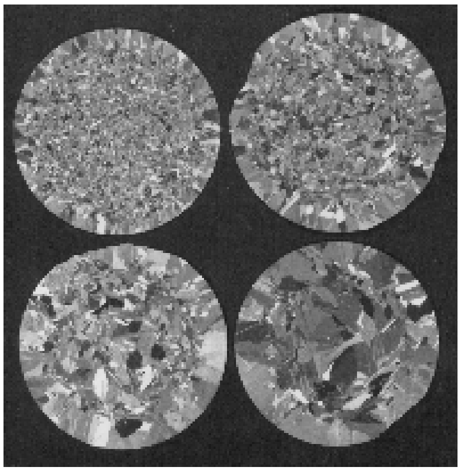


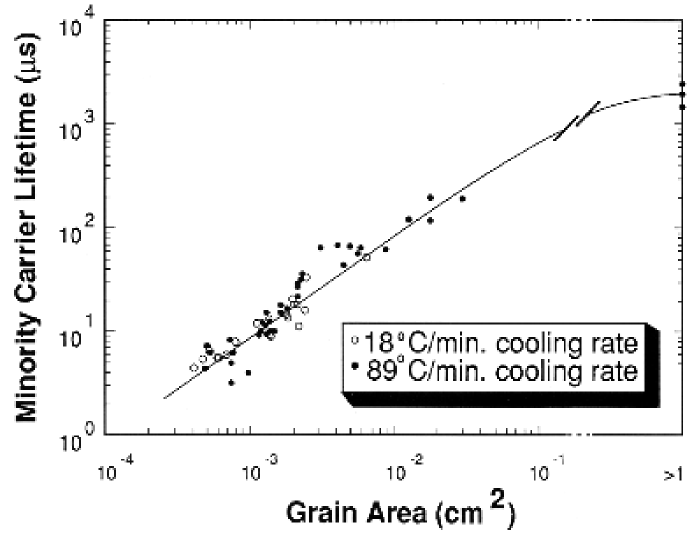




Grain Size Effects on τ and η

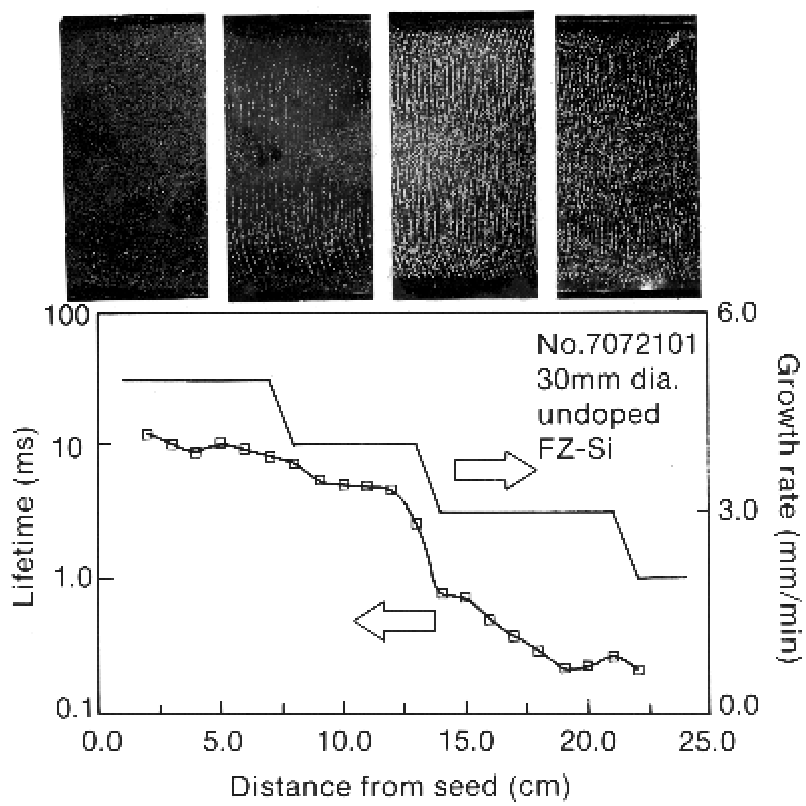
Float zoning with a large diameter and very fine-grained polycrystalline seed, cut along the diameter of a CVD-grown polycrystalline feedstock log, was used to generate a set of high-purity samples with increasing grain size. Wafer lifetimes were measured and correlated with grain size and the results are shown below. Grids of 2-mm-square diagnostic mesa solar cells were also fabricated and correlated with grain size.





Type A and B Swirl Effects on τ

As the growth rate of FZ dislocation-free (DF) crystals increases, the incidence of grown-in type A and type B swirl defects decreases and at a threshold rate (~ 4mm/min for the 30-mm-dia. example shown here) swirl defects are eliminated leaving only type D or type I microdefects. The elimination of swirl defects has a remarkable effect on τ - more than an order of magnitude increase in τ, from 0.5 to 10 ms, as the growth rate increases from 2 to 5 mm/min. The decrease of swirl defects (and accompanying increase in τ) appears to be related to an increase in v/G, where v is the growth rate and G is the thermal gradient in the crystal near the solid/ liquid interface.



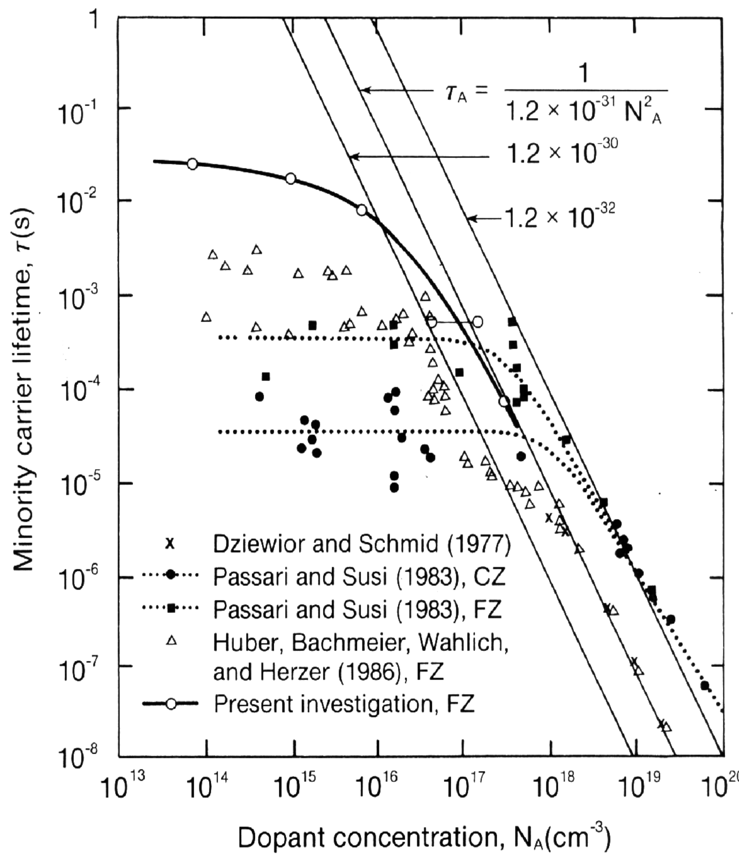
Cooling Rate Effect on τ

Besides growth rate, the crystal cooling rate (approximately equal to the product v x G) also has an effect on τ. When all swirl defects are eliminated by growing dislocation-free FZ crystals at an adequately fast v/G, it is observed that higher τ is observed at slower cooling rate. The dependence is monotonic, as shown in the abstract, and may be related to some type of frozen-in defect. Fortunately as crystal diameter increases, G tends to decrease as well and higher lifetimes are favored both from swirl defect considerations and cooling rate considerations.

Dopant Effects on τ (Auger Recombination)

High-purity FZ crystals were grown with varying dopant concentrations and under conditions that precluded microdefect swirl formation and fast-cooling defects. Lifetimes as high as 20,000 μsec resulted, and the sample set was used to obtain τ vs. dopant (in this case, Ga) density in this high-τ regime.

We have also examined B, In, and Al p-type dopants, and in general find higher lifetimes for Ga and B than for the other two.



Iron Effect on τ

We used the pill doping method to obtain axially uniform concentrations of Fe at various doping levels in high-purity multicrystalline float-zoned silicon ingots. Both Fe content and grain size have an effect on lifetime, as indicated in the graphical results of the abstract figure. Current work is being extended to single crystal material, and also to a study of combined Fe doping and p-type electrically active doping in controlled float-zoned samples.

Nitrogen Effect on τ

We float-zoned both dislocation-free single crystalline and multicrystalline silicon ingots in ambients with varying amounts of nitrogen in argon. In the case of dislocation-free crystals grown at 3 mm/min, a small amount of N in the Ar ambient is observed to eliminate A and B type swirl defects, relative to growth at the same speed in pure argon. Lifetimes were higher in the swirl-free portion grown with some nitrogen. In the case of multicrystalline ingots, growth in high (even 100%) N_2 ambients did not appreciably degrade lifetime. However, a nitride skin formed on the melt in this case.

Summary

A few examples of the types of defect and impurity studies that can be done with controlled silicon samples generated by the FZ method have been given. Many other types of controlled samples could be generated this way (e.g. Fe in Si with or without dislocations, highly defected vs normal grains in multicrystalline Si material, effects of O or C in Si on τ, etc.).